



Electrochemical investigations of copper behaviour in different cupric complex solutions: Voltammetric study

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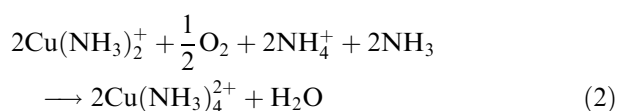
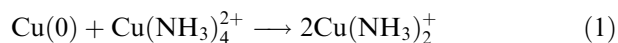
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Abstract

The electrochemical behaviour of copper has been investigated in different cupric complex solutions by cyclic voltammetry. In pyridinic and picolinic solutions the reduction of cupric complex occurred in two stages leading to Cu(I) and Cu(0), respectively. The electrodeposited copper is oxidized in two steps leading to Cu(I) and Cu(II) as in ammoniacal cupric complex solutions. In glycine, alanine, sulfamic acid and ethylenediamine solutions, the cuprous complex is an intermediate in the cupric complex reduction but it is not detected during the oxidation of the electrodeposited copper in these solutions. In EDTA and triethanolamine solutions, the cuprous complex is not observed. The rate of copper etching was determined in pyridinic and ammoniacal cupric solutions and was shown to be faster in ammoniacal cupric solutions than in the pyridinic solutions.

1. Introduction

In the manufacture of printed circuit boards, copper etching is generally carried out in ammoniacal solutions. The process involves copper oxidation by an ammoniacal cupric complex (Equation 1). The cuprous complex formed is oxidized by oxygen to regenerate the cupric complex (Equation 2):



The ammonia evaporates during etching and also during the regeneration of spent solutions which requires adding ammonia to the etching solutions. This involves an additional cost. It is therefore essential to substitute ammonia with nonvolatile complexing agents of copper in order to find new etching solutions. Compounds, such as glycine, alanine, sulfamic acid, pyridine, picoline, triethanolamine and ethylenediamine, were chosen because of their strong complexing properties of nitrogen towards copper.

The electrochemical behaviour of glycine, alanine and ethylenediamine complexes has been investigated for both reduction and oxidation [1–8]. The redox potential of cupric complexes in ammoniacal, triethanolamine, ethylenediamine and EDTA solutions was also determined [9–11]. The roles of pH and Cu(II) concentration in the electrodeposition of Cu in NH_4Cl solutions has been investigated [12]. Copper etching by the cupric ammoniacal complex has been the subject of some works [13, 14]. Larin et al. [13] have shown that the electrochemical processes are accompanied by chemical dissolution the products of which are CuCl and CuO . Previously, we employed cyclic voltammetry to investigate the mechanism of copper etching in ammoniacal solutions [14]. To our knowledge, however, the copper etching by nonammoniacal cupric complexes has never been the subject of a study in the literature. The aim of this work, therefore, is to investigate the electrochemical behaviour of several cupric complexes for comparison with our previous work in ammoniacal solutions [14] and to determine whether their oxidizing properties lead to the metallic copper etching. The etching rate of copper by cupric ammoniacal and pyridinic complexes is also determined.

2. Experimental details

2.1. Chemicals

Solutions were prepared with commercially available chemicals (Aldrich and Fluka). The electrolytic and etching solutions were obtained by copper sulfate dissolution ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$) in the complexing agent solutions. The pH of the latter was previously adjusted to 10 with Na_2CO_3 in the amino acids case or to the $\text{p}K_a$ values of the other compounds with HCl or Na_2CO_3 .

2.2. Procedures

Voltammetric experiments were carried out using commercial instrumentation (PAR, model 362). Data were recorded on a Kipp and Zonen X-Y recorder. A conventional three-electrode cell (used with a saturated calomel electrode (SCE) as reference electrode) was placed in a Luggin capillary and a graphite rod used as the counter electrode. The working electrode was a disc of vitreous carbon (dia. 3 mm). The electrode was polished with emery paper up to grade 4000 and then rinsed with distilled water before use. Potentiodynamic tests were conducted at a scan rate of 50 mV s^{-1} .

The copper etching rate was determined from the weight loss of the copper samples after their immersion in shaken etching solutions. The sample was twisted copper wire (99.99%; dia. 2 mm), 10 cm long for the part immersed in the solution.

All experiments were carried out at room temperature under a nitrogen atmosphere.

3. Results and discussion

3.1. Voltammetry of cupric complexes

The complexing agent and Cu(II) concentrations were between 0.5 M to 1 M and 10^{-3} M to 5×10^{-2} M, respectively. The cupric complexes are stable in every complexant medium and are studied in potential domain where the complexing agent solutions are inactive. The complexing agent solutions are described together when their cyclic voltammograms are similar.

3.1.1. Pyridinic and picolinic cupric solutions

The cyclic voltammogram in Figure 1 shows two cathodic peaks C1 and C2 and two anodic peaks A2 and A1. The cathodic and anodic peaks potential in the two solutions are given in Table 1.

The cathodic peak C1 can be attributed to the reduction of the cupric complex to cuprous complex which is then reduced to metallic copper (peak C2). Potential displacement of the peak C2 towards the positive potential occurs at the second potential scan or when the copper deposit on the electrode was increased by potentiostatic polarization at -0.9 V vs SCE . The peak C2 potential depends on the electrode/electrolyte

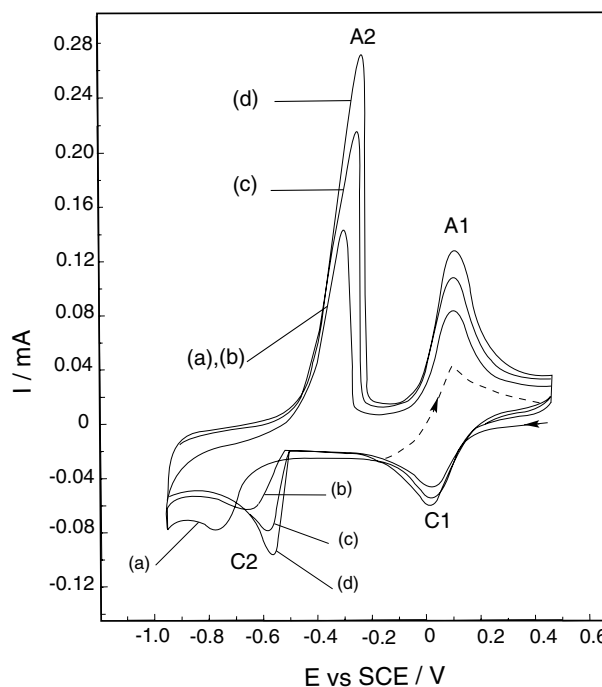


Fig. 1. Cyclic voltammetry of cupric complex (5×10^{-3} M) in solution of pyridine (1 M)/ HCl (0.5 M) at stationary vitreous carbon electrode (a) first scan; - - - reversing scan from -0.1 V vs SCE ; (b) second scan; (c) anodic scan after 15 s of halt at -0.9 V vs SCE ; (d) anodic scan after 30 s of halt at -0.9 V vs SCE .

interface. The shape of the peak A2 is characteristic of redissolution phenomenon. It is attributed to the copper deposit oxidation to cuprous complex. The high value of the peak current is due to the redissolution of copper electrodeposited during the forward potential scan. The cuprous complex is oxidized to cupric complex (peak A1). The couple Cu(II)/Cu(I) appears to be reversible and soluble as shown by the current ratio i_{pa}/i_{pc} of the peaks A1 and C1 being close to one. The values of $\Delta E = (E_{A1} - E_{C1})$ close to 0.06 V confirms that the couple Cu(II)/Cu(I) is a monoelectronic system.

When the copper deposit at the second cathodic peak C2 increases (Figure 1, curves (c) and (d)) the currents of the peaks A2 and A1 increase consequently. This confirms that the copper oxidation generates soluble products. The difference between the cathodic and the anodic peaks potential shows that the couple Cu(I)/Cu(o) is a slow system. The voltammetric behaviour of pyridinic and picolinic cupric solutions shows that the reduction of these complexes occurs in two monoelectronic steps followed by electrodeposited copper oxidation in two steps as well. The cuprous complex is stabilized by pyridinic and picolinic compounds. It constitutes an intermediate for the reduction of the cupric complex and for the electrodeposited copper oxidation. The behaviour of pyridinic and picolinic cupric complexes is similar to the ammoniacal one [14]. Indeed, the corrosion potentials of copper in etching solutions correspond to the first oxidation (peak A2) of copper and to the first reduction of cupric complex

Table 1. Values of the cathodic peaks C1, C2 potentials E_{C1} , E_{C2} and the anodic peaks A1, A2 potentials E_{A1} , E_{A2} obtained from cyclic voltammograms for 10^{-3} M Cu(II) in the different solutions at stationary vitreous carbon electrode and with scan potential of 50 mV s^{-1}

| Electrolytic solution /M | | E_{C1} vs SCE /V | E_{A1} vs SCE /V | E_{C2} vs SCE /V | E_{A2} vs SCE /V |
|---------------------------------|-----|-----------------------|-----------------------|-----------------------|-----------------------|
| Ammoniaque | 0.5 | -0.22 | -0.15 | -0.84 | -0.32 |
| NH ₄ Cl | 0.5 | | | | |
| Pyridine | 1 | +0.06 | +0.12 | -0.68 | -0.34 |
| HCl | 0.5 | | | | |
| Picoline | 1 | +0.02 | +0.08 | -0.70 | -0.35 |
| HCl | 0.5 | | | | |
| Alanine | 1 | -0.44 | -0.39* | -1.18 | -0.28 |
| Na ₂ CO ₃ | 1 | | | | |
| Sulfamic acid | 1 | -0.30 | -0.24* | -0.70 | -0.04 |
| Na ₂ CO ₃ | 1 | | | | |
| Glycine | 1 | -0.46 | -0.38* | -0.94 | -0.28 |
| Na ₂ CO ₃ | 1 | | | | |
| Ethylenediamine | 1 | -0.66 | -0.60* | -1.22 | -0.40 |
| HCl | 0.5 | | | | |

* E_{A1} is obtained from cyclic voltammograms when the backward potential scan is inversed just after the peak C1.

(peak C1). Copper oxidation by cupric complex leading to cuprous complex in pyridinic and picolinic solutions appears to be possible.

3.1.2. Amino acids, sulfamic acid and ethylenediamine cupric solutions

The cyclic voltammogram (Figure 2) shows two cathodic peaks C1 and C2 and one oxidation peak A2 when the potential scan is inversed after peak C2. When the potential scan is inversed after the first peak C1, anodic peak A1 is observed (Figure 3, curve (a)). When cathodic polarization is maintained at C1 before potential inversion, anodic peak A2 appears after A1 (Figure 3, curves (b), (c) and (d)). This indicates that there are kinetic complications. The potentials of the cathodic and anodic peaks in the different solutions are

given in Table 1 and show that copper oxidation by these cupric complexes is not possible.

The currents of peaks C1 and A1 are equal and the values of $\Delta E = (E_{A1} - E_{C1})$ are close to 0.06 V indicating that independently of the solution nature and concentration, the system at peaks C1 and A1 is reversible, soluble and monoelectronic couple. This system corresponds to the redox couple Cu(II)/Cu(I). In glycine, alanine, sulfamic acid and ethylenediamine solutions, the cuprous complex is stabilized by the potential at the CV electrode/electrolyte interface and constitutes an intermediate for the reduction of the cupric complex. The cuprous complex formed at the peak C1 is reduced to metallic copper at the peak C2. The electrodeposited copper is oxidized at the peak A2. When potential scan is inversed after cathodic polarization at the peak C1 or after the peak C2, the potential of

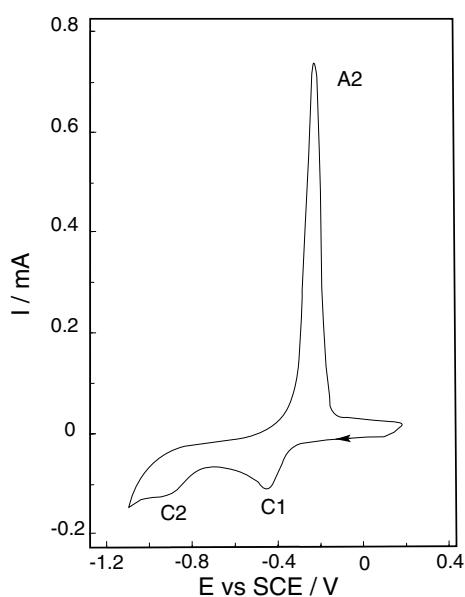


Fig. 2. Cyclic voltammetry of cupric complex (5×10^{-3} M) in solution of glycine (0.5 M)/Na₂CO₃ (0.5 M) at stationary vitreous carbon electrode.

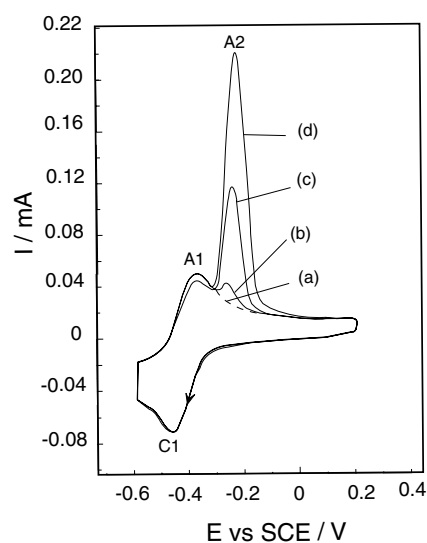


Fig. 3. Cyclic voltammetry of cupric complex (5×10^{-3} M) in solution of glycine (0.5 M)/Na₂CO₃ (0.5 M) at stationary vitreous carbon electrode with increasing time of halt at -0.6 V vs SCE ; (a) 0, (b) 10, (c) 20 and (d) 30 s.

the observed oxidation peak A2 in the two situations has the same value in each considered solution and corresponds to the oxidation of Cu to Cu(II).

(a) *Glycine, alanine and ethylenediamine cupric solutions*
The sharp peak A2 corresponding to redissolution appears after cathodic polarization for different periods of time at a potential of -0.6 V vs SCE before inverting the potential scan (Figure 3). At this potential the current of peak A2 increases with time but there is no significant change for peak A1. This supposes that at this potential there is a contribution of copper electro-deposition which proceeds through a relatively slow reaction.

(b) *Sulfamic acid cupric solutions*

When the potential scan was inverted at potentials ranging from -0.4 to -1 V vs SCE (Figure 4), the voltammogram exhibits the tendency of peak A1 to be masked as soon as the peak A2 appears. The oxidation of cuprous complex may occur on copper. The current peak A2 increases with the variation of potential scan inversion value towards the cathodic values. This confirms that the redissolution peak A2 can be attributed to the oxidation of metallic copper deposit. The anodic current after peak A2 decreases slowly which suggests a slow dissolution of a Cu(II) compound.

3.1.3. EDTA and triethanolamine cupric solutions

The electrochemical behaviour of 5×10^{-2} M EDTA cupric and 5×10^{-2} M triethanolamine cupric complexes was investigated (Figure 5). Cyclic voltammograms show one cathodic peak C and one anodic peak A.

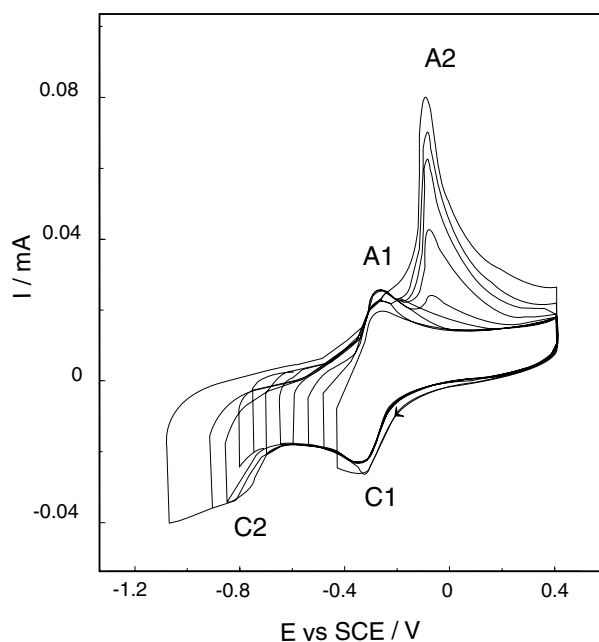


Fig. 4. Cyclic voltammetry of cupric complex (10^{-3} M) in solution of sulfamic acid (1 M)/ Na_2CO_3 (1 M) at stationary vitreous carbon electrode with various reversal potentials during the anodic scan from -0.4 to -1 V vs SCE.

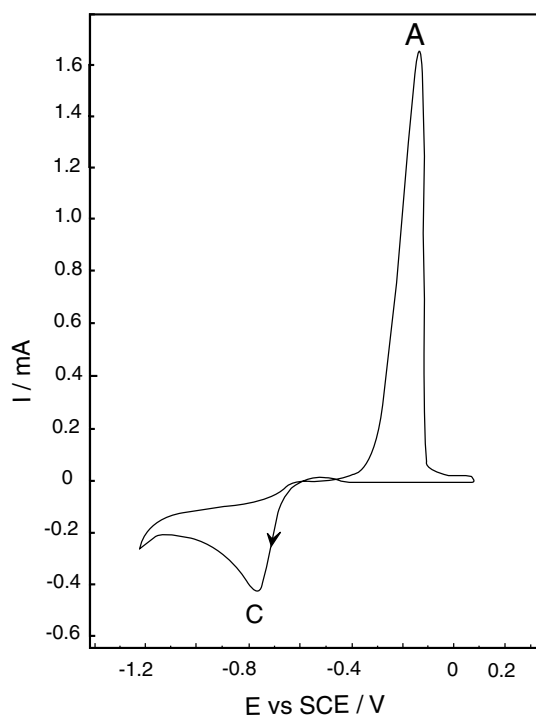


Fig. 5. Cyclic voltammetry of 5×10^{-2} M cupric complex in solution of EDTA (1 M)/HCl (0.5 M) at stationary vitreous carbon electrode.

Table 2. Values of the cathodic peaks C potentials E_C and the anodic peaks A potentials E_A obtained from cyclic voltammogram for 5×10^{-2} M Cu(II) in EDTA and triethanolamine solutions at stationary vitreous carbon electrode and with scan potential of 50 mV s^{-1}

| Electrolytic solution /M | | E_C vs SCE /V | E_A vs SCE /V |
|--------------------------|-----|-----------------|-----------------|
| EDTA | 1 | -0.94 | -0.26 |
| HCl | 0.5 | | |
| Triethanolamine | 1 | -0.62 | -0.14 |
| HCl | 0.5 | | |

Values of cathodic and anodic peak potentials C and A are given in Table 2. The peak A is characteristic of redissolution phenomenon. The cupric complex reduction occurs in one stage at the peak C. Then the peak C corresponds to cupric complex reduction to metallic copper which is reoxidized to cupric complex. The current integration indicates that at peak A the oxidation of electrodeposited copper to cupric complex is complete.

In EDTA and triethanolamine solutions, the reduction of cupric complex to copper and the oxidation of metallic copper occur both in one stage. These ligands do not stabilize Cu(I). Thus, it appears from the voltammetric study that copper oxidation by these cupric complexes is not possible.

3.2. Etching rate of copper

The etching rate of copper was carried out in ammoniacal cupric solutions with high Cu(II) concentration close to the industrial one and in saturated

Table 3. Cu(II) concentration and corresponding etching rate value of copper oxidation by cupric ammoniacal solution and cupric pyridinic solution

| Etching solution /M | Cu(II) concentration /g l ⁻¹ | | Rate /μm h ⁻¹ |
|------------------------------------|--|-----|-----------------------------|
| NH ₃ , H ₂ O | 3 | 100 | 482 |
| NH ₄ Cl | 3 | | |
| Pyridine | 1 | 76 | 4.1 |
| HCl | 0.5 | | |

pyridinic cupric solution. The Cu(II) concentration of picolinic cupric solution was too low ($<1 \text{ g l}^{-1}$) to be considered. Table 3 shows the Cu(II) concentration and the corresponding etching rate value. The etching rate was calculated after immersion of copper during one minute in ammoniacal cupric solution and during one hour in pyridinic cupric solution to reach significant weight loss. The difference of time of immersion is explained by the fact that etching is too fast in ammoniacal solutions. The etching rate of copper in pyridinic cupric solution is lower compared to the one in ammoniacal solution probably because of the poor Cu(II) solubility in pyridinic solutions.

4. Conclusion

The cyclic voltammetric behaviour of the cupric complexes depends strongly on the complexing nitrogen compounds. In glycine, alanine, sulfamic acid and ethylenediamine solutions the cuprous complex is an intermediate in the cathodic reduction of the cupric complex but it is not detected during the anodic

oxidation of the electrodeposited copper. In EDTA and triethanolamine solutions the cuprous complex is not observed. The pyridinic and picolinic cupric complexes can oxidize the metallic copper to produce the corresponding cuprous complex and then play the same role as ammonia. However, the very poor solubility of Cu(II) in picolinic solution inhibits the copper oxidation process and the corrosion rate of copper etching in pyridinic cupric solution remains to be improved.

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